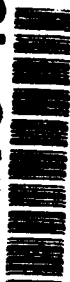


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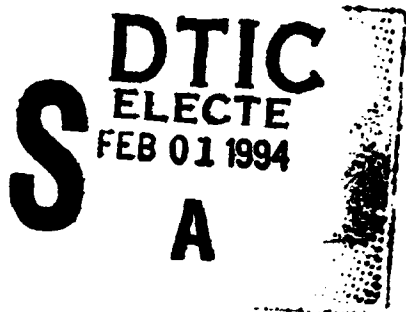
Synthesis and Neutron Diffraction Study of  $\text{Na}_3\text{WN}_3$  and  $\text{Na}_3\text{MoN}_3$

by

P. E. Rauch, F. J. DiSalvo, N. E. Bresee, D. Partin  
and M. O'Keeffe

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Cornell University  
Department of Chemistry  
Ithaca, NY 14853

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# Synthesis and Neutron Diffraction Study of $\text{Na}_3\text{WN}_3$ and $\text{Na}_3\text{MoN}_3$

P. E. Rauch and F. J. DiSalvo\*

Dept. of Chemistry, Cornell University, Ithaca, NY 14853

N. E. Brese, D. Partin and M. O'Keeffe

Dept. of Chemistry, Arizona State University, Tempe, AZ 85287

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\*Author to whom correspondence should be addressed.

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## ABSTRACT

We have extended our ambient pressure method for the synthesis of ternary alkali metal nitrides to synthesize a new class of nitrides,  $\text{Na}_3\text{MN}_3$  (M=Mo or W). These compounds were synthesized from the metal nitride and  $\text{NaNH}_2$  at  $500^\circ\text{C}$  under flowing ammonia at atmospheric pressure. The structures were examined using X-ray powder diffraction and neutron powder diffraction, and found to be identical with that obtained from single crystal prepared by Ostermann, Zachwieja and Jacobs at high pressure.

With our discovery of ambient pressure syntheses of the alkali metal tantalum nitrides and the previously unreported niobium analogs(1) we have continued our investigation to see if other alkali metal transition metal nitrides could be formed. We report here syntheses and powder diffraction studies of two alkali metal transition metal nitrides,  $\text{Na}_3\text{WN}_3$  and  $\text{Na}_3\text{MoN}_3$ , made as polycrystalline powders at ambient pressure. We were not able to solve the structure of these two compounds until we used the recently reported single crystal structure of  $\text{Na}_3\text{MoN}_3$ , synthesized under high pressure ammonia, as a starting point for the refinements(2).

## EXPERIMENTAL

All X-ray powder diffraction patterns were taken on an XDS 2000 powder diffractometer (Scintag inc., Santa Clara, CA) using  $\text{Cu K}\alpha$  radiation. Time-of-flight neutron diffraction data were collected at room temperature on the High Intensity Powder Diffractometer (HIPD) of the LANSCE facility at Los Alamos National Laboratory. Data from the  $2\theta = \pm 153^\circ$  and  $\pm 90^\circ$  detector banks were refined with the Generalized Structure Analysis System (GSAS)(3), a Rietveld profile analysis code(4). The minimum d-spacing included in the refinements was 0.66 Å unless otherwise stated. Below this point, the profiles were featureless because the reflections were broad, and more than 350 reflections contributed to each profile point.

Starting materials,  $\text{WO}_3$  ( 99.99%, Atomergic, Farmingdale, NY) and  $\text{MoO}_3$  (99.9%, Cerac, Milwaukee, WI) were used as received, without further purification. Sodium metal (99.9%, Strem, Newburyport, MA) was washed three times with hexane. All reagents and products were stored and manipulated in an argon filled glove box, unless otherwise noted.

$\text{W}_2\text{N}$  was synthesized by reduction of  $\text{WO}_3$  using dry ammonia gas. In the ammonia flow,  $\text{WO}_3$  was heated to  $700^\circ\text{C}$  over 6 hours and then left at  $700^\circ\text{C}$  for 11 hours. X-ray powder diffraction showed the product to be approximately 95%  $\text{W}_2\text{N}$ , the remainder being tungsten metal.  $\text{Mo}_2\text{N}$  was synthesized in a fashion similar to  $\text{W}_2\text{N}$ (5). X-ray powder diffraction showed only  $\text{Mo}_2\text{N}$ .

$\text{Na}_3\text{WN}_3$  was synthesized from sodium metal and  $\text{W}_2\text{N}$  in three steps. The first step forms the  $\text{Na}_3\text{WN}_3$  and removes most of the excess  $\text{NaNH}_2$  by sublimation. The second step removes the last traces of  $\text{NaNH}_2$ , and also causes the  $\text{Na}_3\text{WN}_3$  to lose some of its sodium. The final step replaces the small sodium deficiency of the  $\text{Na}_3\text{WN}_3$ , through the gas phase, and therefore does not introduce any excess  $\text{NaNH}_2$ .

Typically, 3.84 g (0.0101 moles) of  $\text{W}_2\text{N}$  was loaded into a large alumina boat. An excess of sodium metal, with the thin oxide coat cut away, typically 3.65 g (0.159 moles), was also placed into the alumina boat. A small piece of sheet copper metal was placed completely over the boat, to prevent any devitrified

pyrex or quartz from falling into the reaction mixture. This assembly was placed into a pyrex tube, and then allowed to react with dry ammonia gas, as previously described. The reaction mixture was quickly heated to 50°C, and then over 1 hour, heated to 350°C, to begin the formation of  $\text{NaNH}_2$  from the sodium metal and the ammonia gas. Over the next 3 hours the sample was heated to 500°C, to complete the formation of the  $\text{NaNH}_2$ . Next, the sample was allowed to soak at 500°C for 8 hours, to complete the formation of  $\text{Na}_3\text{WN}_3$ . Finally the sample was allowed to cool in the furnace.

In the second step, the alumina boat, with the copper shield, was moved to a quartz tube and again allowed to react with dry ammonia gas. The sample was immediately heated to 50°C, and over the course of 2 to 3 hours heated to 600°C, then left to soak at 600°C for 8 hours, and finally cooled in the furnace.

In the final step, the alumina boat with the copper shield, was moved to a pyrex tube. A small piece of oxide free sodium metal (~0.4 g) in an alumina boat was placed upstream of the reaction mixture. With dry ammonia gas flowing, the sample was immediately heated to 50°C, and over the course of 1 hour heated to 350°C, and then heated to 500°C over the next 3 hours.  $\text{NaNH}_2$  then sublimed over the main reaction mixture for 8 hours at 500°C. Finally, the reaction mixture was allowed to cool in the furnace.

The final product is bright yellow, and the X-ray powder diffraction pattern shows only a very small amount of WN (less than 1%) as an impurity. Neutron powder diffraction also found traces of minor phases. Elemental analysis was performed by atomic emission from an inductively coupled plasma (ICP)<sup>1</sup>.

The Na<sub>3</sub>MoN<sub>3</sub> is made in the same manner as Na<sub>3</sub>WN<sub>3</sub>, using Mo<sub>2</sub>N instead of W<sub>2</sub>N, except that before the final step, the sodium deficient Na<sub>3</sub>MoN<sub>3</sub> was ground in a mortar and pestle. The final product is maroon red, and again, the X-ray powder diffraction pattern shows only a very small amount of MoN (less than 1%) as an impurity.

## RESULTS AND DISCUSSION

The syntheses of Na<sub>3</sub>WN<sub>3</sub> and Na<sub>3</sub>MoN<sub>3</sub> are significantly more complex than that of NaTa<sub>2</sub>N<sub>2</sub> or KTa<sub>2</sub>N<sub>2</sub>. As previously described(1), the syntheses of NaTa<sub>2</sub>N<sub>2</sub> and KTa<sub>2</sub>N<sub>2</sub> consist of a single step, combining the formation of the alkali metal amide, synthesis of the product phase, and removal of any excess alkali metal amide. With Na<sub>3</sub>WN<sub>3</sub> and Na<sub>3</sub>MoN<sub>3</sub>, the first two steps are combined, but the removal of the excess alkali metal amide is not as simple, for two reasons. First, all the excess amide cannot be removed at 600°C in a reasonable period of time, without removing the reaction mixture from the original reaction tube. The reasons for this are not completely clear, but may have to do with the inclusion of the copper shield, and the reduced



temperature of amide removal, both combining to reduce the rate of amide sublimation. By removing the reaction mixture to a clean tube, any previously sublimed amide is eliminated, apparently increasing the initial sublimation rates.

The second complicating factor is that all the excess alkali metal amide cannot be sublimed out without a simultaneous loss of sodium from  $\text{Na}_3\text{WN}_3$  and  $\text{Na}_3\text{MoN}_3$ . Hence, once all the amide is removed, the lost sodium must be replaced by a gas phase reaction. If the amide is removed at higher temperatures ( $700^\circ\text{C}$ ), then either too much sodium is lost to replace by a gas phase reaction, or the sodium loss is simply irreversible.

These compounds can also be synthesized from the corresponding transition metal and sodium amide. As in the case of  $\text{MM}'\text{N}_2$  ( $\text{M}=\text{Na}$  or  $\text{K}$ ,  $\text{M}'=\text{Ta}$  or  $\text{Nb}$ )(1), the newly forming compound blocks further reaction with the interior of the metal particle, preventing complete reaction without many grinding and re-reaction steps. It should be noted, however, that even with the use of the transition metal nitride, a small amount of unreacted nitride is still found. Unlike  $\text{LiMoN}_2$  these phases could not be synthesized from oxide precursors,  $\text{Na}_2\text{WO}_4$  or  $\text{Na}_2\text{MoO}_4$ , under flowing ammonia(6). Rather these oxide precursors form oxynitrides,  $\text{Na}_3\text{MO}_3\text{N}$  ( $\text{M}=\text{W}$  or  $\text{Mo}$ )(7).

Ostermann, Zachwieja, and Jacobs recently reported the structure of  $\text{Na}_3\text{MoN}_3$ (2) (Table I), and this was used as a starting model in our studies. It was expected that the N positions and

displacement parameters from a neutron structure determination would be more reliable. However, the low symmetry and broad peaks exhibited by this material, probably caused by small particle size, precluded a definitive structural determination.

Several refinement schemes were employed. The background was modelled using a cosine series, and the peak shapes were modelled using the Von Dreele-Jorgensen-Windsor function(8). In addition, the diffractometer zero points, lattice parameters, and absorption coefficients(9,10) were included in the refinements. The results of several attempts are listed in Table II.

We first tried a fixed-model refinement based on the previous structure determination(2). Only the lattice parameters, background coefficients, diffractometer zero point, and the Gaussian width of the peaks ( $\sigma_1$ ) were refined. This refinement converged and served as a reference; that is, it measures how well the known structure of  $\text{Na}_3\text{MoN}_3$  matches our neutron data for  $\text{Na}_3\text{WN}_3$ . The residuals  $\chi^2 = 3.195$ ,  $wRp = 0.071$ , and  $Rp = 0.048$  as well as the observed and calculated histograms (see Fig. 1) are generally acceptable. However, an analysis of the residuals revealed poor agreement of the observed and calculated intensities for reflections with d-spacings lower than  $0.75\text{\AA}$  (a region from which much of the structural information is derived). In addition, Fourier difference peaks as high as 5% of a N atom (30% of a Na atom) were observed.

A structure refinement with isotropic displacement parameters linked together by atom type resulted in negative  $U_{iso}$  values for both Na and W atoms. A fully free refinement left three of the fourteen  $U_{iso}$  values farther than  $2\sigma$  away from positive. In addition, the structural models obtained included W-N and Na-N bond lengths as short as 1.66 Å and 2.12 Å, respectively.

The X-ray scattering lengths of Na and N are much smaller than Mo and W. Therefore, we tried to refine several models in which the positions of the W atoms were fixed at the values for Mo determined in the X-ray diffraction experiments.

In the first refinement, we held the W positional parameters fixed, and refined an overall  $U_{iso}$  value. The  $U_{iso}$  value refined to an acceptable value of 0.0137(6), however, short Na-N distances were again obtained (minimum of 2.24Å), although the W-N distances were more acceptable (1.70-2.05Å).

A refinement in which the W positional and displacement parameters were fixed but all other parameters were unconstrained resulted in two negative  $U_{iso}$  values. Unacceptably-short Na-N distances were also obtained (minimum of 2.06Å).

These refinements were all unstable and required considerable damping in the beginning cycles. Convergence was achieved slowly. The diffraction profiles are rather broad. Most of the structural information is obtained from peaks in the low d-spacing ranges, and there is considerable overlap of reflections in

these regions (up to 350 peaks contributed to a single profile point) due to the low crystallographic symmetry. This problem was exacerbated by the presence of some unidentified minor phases. Therefore, we were not able to improve upon the structural information obtained in the previous X-ray diffraction experiment.

The most notable features of the structure of  $\text{Na}_3\text{WN}_3$  are the continuous chains of  $\text{WN}_4$  tetrahedra (see Fig. 2). The two bridging N atoms (shared between tetrahedra) form long bonds to the W atoms, while the terminal N atoms form relatively short (strong) bonds, as one expects from classical ideas of crystal chemistry. Ostermann has noted that the  $\text{WN}_4$  chains may be described with the Zintl-Klemm concept(2).

The bond-valence method has been promoted as a tool for crystal chemists(11) and has been applied to nitrides(12). The basic tenet of the method is that associated with each bond length is a unique bond valence (strength) such that the sum of all the individual bond valences is equal to the atom's total valence. This method of partitioning of an atom's bonding power into individual bonds makes use of an empirical equation to quantify bonding in crystals. Bond valence parameters appropriate to nitrides are available(13), and we have applied them to the structure of  $\text{Na}_3\text{MoN}_3$ .

At first glance, the tetrahedra in  $\text{Na}_3\text{WN}_3$  might be expected to contain W-N bonds of  $3/2$  valence units (v.u.), since the sum at

W would then be 6 v.u. This assignment would leave the bridging N atoms with a sum of 3 v.u. and the terminal N atoms each with a bonding of  $3/2$  v.u. to form Na-N bonds. However, the Na atoms use some of the bonding power of the bridging N atoms, thus weakening the W-N bonding. To maintain a total of 6 v.u. for the W atoms, the bonding to the terminal N atoms is strengthened ( $v(\text{terminal}) = 1.90\text{--}2.00$  v.u.,  $v(\text{bridging}) = 1.25\text{--}1.40$  v.u.). A complete listing of bond valences and electrostatic energies (calculated using the method of Ewald<sup>(14)</sup>) is given in Table III. The average deviation of the valences from their expected values is excellent<sup>2</sup>.

We attempted to optimize the structure of  $\text{Na}_3\text{MoN}_3$  subject to bond valence and bond length constraints using the DVLS program<sup>(15)</sup>. However, as expected from the good match of valence sums and expected valences, the structural model changed insignificantly. A "better" starting model for the refinements is, therefore, not available.

The structure is somewhat surprising from the stoichiometry given that the favored coordination environment for N is an octahedron<sup>(12)</sup>. The coordination numbers  ${}^{iv}\text{Na}_3{}^{vi}\text{W}{}^{vi}\text{N}_3$  would offer a more symmetrical structure than the observed  ${}^v\text{Na}_2{}^{iv}\text{Na}{}^{iv}\text{W}{}^{vi}\text{N}_3$ , where the preceding roman numerals in superscript indicate coordination number. This observation suggests that the role of Na in the compound is not one of passive electron donor but rather one of active participant in the bonding.

In the only other tungsten (VI) and molybdenum (VI) nitrides known,  $\text{Ba}_3\text{MN}_4$  ( $\text{M}=\text{Mo}$  or  $\text{W}$ ), the transition metal is also tetrahedrally coordinated, but these tetrahedra are isolated(16). In  $\text{Ca}_3\text{CrN}_3$  the chromium atom is only trigonally coordinated(17). Another interesting comparison is one with oxides. Many ternary oxides of molybdenum (VI) and tungsten (VI) contain the transition metal in a tetrahedral site, such as  $\text{CaMoO}_4$  (sheelite structure),  $\text{Li}_2\text{WO}_4$  (phenacite structure) and  $\text{Cs}_2\text{WO}_4$  ( $\beta$ - $\text{K}_2\text{SO}_4$  structure)(18). On the other hand, it is interesting to note that in the more covalent binary oxides,  $\text{MoO}_3$  and  $\text{WO}_3$ , the transition metal is octahedrally coordinated by oxygen. Perhaps if " $\text{WN}_2$ " or " $\text{MoN}_2$ " could be made, the transition metal might be 6-fold coordinated.

It should be noted that we have not simply substituted ammonia at ambient pressure for *nitrogen* at high pressure, but rather for *ammonia* at high pressure. This shows that  $\text{Na}_3\text{MoN}_3$  and  $\text{Na}_3\text{WN}_3$  (like  $\text{KTaN}_2$  and  $\text{NaTaN}_2$  (1)) are not high pressure phases kinetically trapped at low pressure. In many cases it appears that high pressure is not necessary to prepare phases first reported using this method. High pressure, however, does seem to stabilize these phases at higher temperature, and this may be why previous preparations (2) have yielded larger crystals. The broad peaks exhibited by this material with atmospheric pressure preparation are likely caused by small crystallite size.

## CONCLUSION

By extending our ambient pressure method for the synthesis of ternary alkali metal nitrides we have synthesized  $\text{Na}_3\text{WN}_3$  and  $\text{Na}_3\text{MoN}_3$  from the corresponding metal nitride and  $\text{NaNH}_2$  at  $500^\circ\text{C}$ , under flowing ammonia. We have also confirmed the previously reported<sup>2</sup> structures of these compounds using neutron diffraction. Finally, we have examined the structures of these compound by using the bond-valence method and by comparison to other related compounds.

## ACKNOWLEDGEMENT

We greatly appreciate the support of the Office of Naval Research. We would also like to thank Mike Rudsky for assistance with the elemental analysis.

**Table I** Atomic positions and neutron scattering lengths of  
 $\text{Na}_3\text{MoN}_3$  (2).

Space Group Cc, Z = 8, a=13.854(5)Å, b = 10.889(2)Å, c = 6.366(2)Å, $\beta$ = 117.23(3)°					
Position	Atom	x	y	z	b (10 <sup>-12</sup> cm)
4a	Mo(1)	0	0.23793(8)	0	0.66
4a	Mo(2)	0.25034(9)	0.2511(1)	0.5752(2)	0.66
4a	N(1)	0.004(1)	0.393(1)	0.906(3)	0.94
4a	N(2)	0.022(1)	0.126(2)	0.822(4)	0.94
4a	N(3)	0.242(1)	0.384(2)	0.735(3)	0.94
4a	N(4)	0.2920(9)	0.127(1)	0.781(2)	0.94
4a	N(5)	0.605(1)	0.285(1)	0.823(3)	0.94
4a	N(6)	0.356(1)	0.290(2)	0.469(4)	0.94
4a	Na(1)	0.4918(5)	0.2163(5)	0.015(1)	0.35
4a	Na(2)	0.3806(6)	0.0206(6)	0.578(1)	0.35
4a	Na(3)	0.6249(5)	0.0201(5)	0.814(1)	0.35
4a	Na(4)	0.2379(7)	0.2483(8)	0.037(2)	0.35
4a	Na(5)	0.6173(5)	0.5256(6)	0.628(1)	0.35
4a	Na(6)	0.3641(7)	0.4864(9)	0.120(2)	0.35



**Table II** Refinement schemes.

Feature of refinement	Variables	Rp	wRp	$\chi^2$
No model refined	66	0.048	0.071	3.195
U linked by atom type	111	0.034	0.052	1.808
Fixed W positions	114	0.036	0.057	2.105
Fixed W, overall U	103	0.038	0.061	2.121
Completely free	122	0.033	0.052	1.775

**Table III** bond valences and electrostatic energies.

Atom	$\Sigma v_i$	Madlung potential (V)
Na(1)	0.73	-10.98
Na(2)	1.04	-14.22
Na(3)	0.94	-13.47
Na(4)	0.79	-10.44
Na(5)	0.94	-13.41
Na(6)	0.95	-13.70
Mo(1)	6.64	-61.47
Mo(2)	6.53	-60.93
N(1)	2.90	33.60
N(2)	3.15	34.52
N(3)	2.96	33.72
N(4)	3.20	34.49
N(5)	3.14	41.64
N(6)	3.20	41.62

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## FIGURE CAPTIONS

Figure 1. Observed (+) and calculated (solid line) histograms from a fixed-model refinement based on the previous structure determination(2). The difference profile at the bottom of the figure is on the same scale.

Figure 2. View of  $\text{Na}_3\text{WN}_3$  looking down the b axis. The shaded circles represent sodium atoms. The vertices of the tungsten-centered tetrahedra represent nitrogen atoms.

## FOOTNOTES

1. The elemental analysis gave tungsten 64.5% (62.4% expected) and nitrogen 14.1% (14.3% expected). The sodium content was found to be 27.9% (23.4% expected). Because the sodium value is high, without a simultaneous reduction of the nitrogen and tungsten values, and because of the ubiquitous nature of sodium, we have discounted its anomalously high value.

2.  $\left( \left\langle \frac{|v - \sum v_i|}{v} \right\rangle = 0.08 \right)$